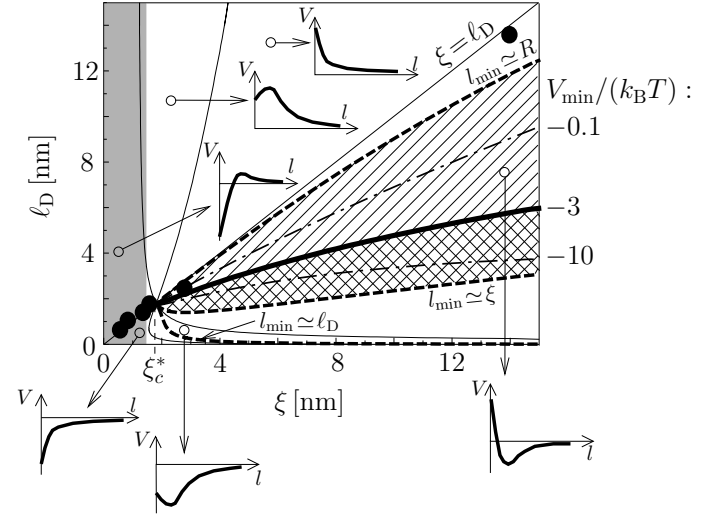


Colloidal aggregation and critical Casimir forces

A recent Letter [1] reports the experimental observation of aggregation of colloidal particles dispersed in a liquid mixture of heavy water (HW) and 3-methylpyridine (MP). The authors claim that the experimental data can be explained in terms of a model which accounts solely for the competing effects of the inter-particle electrostatic repulsion and the attractive critical Casimir force, the decay lengths of which are set by the Debye screening length ℓ_D and the correlation length ξ of the liquid mixture, respectively. Here we show, however, that the reported aggregation actually occurs within ranges of values of ξ and ℓ_D ruled out by the proposed model and that most of the experimental data presented in Fig. 4(c) of Ref. [1] cannot be consistently interpreted in terms of such a model.

Following Ref. [1], the effective potential $V(l)$ of the force acting on two identical colloids of radius $R = 0.2 \mu\text{m}$ and surface charge $\sigma = 2.72 \mu\text{C}/\text{cm}^2$ consists of an electrostatic part $V_{\text{el}}(l) = [2\pi R\sigma^2\ell_D^2/(\varepsilon\varepsilon_0)]e^{-l/\ell_D}$ plus the critical Casimir part $V_C(l) = -k_B T\pi A(R/\xi)e^{-l/\xi}$ [2], where l is the surface-to-surface distance of the two colloids, ε the dielectric constant of the mixture, $A = 1.2$ – 1.5 a universal constant [2] (set to 2 in Ref. [1]), and T the temperature. The expressions for V_{el} and V_C (valid within the Derjaguin approximation $l \ll R$ [2, 3]) have been derived assuming $l \gtrsim \ell_D$ and $l \gtrsim \xi$, respectively, with $\xi \simeq \xi_0(1 - T/T_c)^{-\nu}$ and $\nu \simeq 0.63$, which is expected to hold for $\xi \gg \xi_0$, *i.e.*, sufficiently close to the critical point at temperature T_c . For the present mixture $T_c \simeq 310 \text{ K}$, $\xi_0 \simeq 3 \text{ \AA}$ [4], and therefore significant (non-universal) corrections to V_C are expected to occur within the gray area in the figure, corresponding to $\xi \lesssim 5\xi_0$. Adding NaCl to the mixture causes both a reduction of ℓ_D [1] and a screening of σ . The effective value σ^* which replaces σ in V_{el} can be determined via the Grahme equation [3], which yields $\sigma^* = \sigma g(\ell_D/\ell_\sigma)$ where $g(\rho) = 2/(1 + \sqrt{1 + \rho^2/4})$ and $\ell_\sigma \equiv k_B T \varepsilon \varepsilon_0 / (e\sigma) \simeq 0.2 \text{ nm}$ for a near-critical temperature $T \simeq T_c$ and $\varepsilon \simeq 26$. This value of ε for the mixture with critical MP mass fraction $x_c \simeq 0.29$ [4] (*i.e.*, volume fraction $\phi_c \simeq 0.32$ [7]) is estimated on the basis of the dielectric constants of pure HW (78.3) and MP (10.0) at $T \simeq 298 \text{ K}$ [6] via the Clausius-Mossotti formula, neglecting the fractional volume change (see, *e.g.*, Ref. [5]). The various forms of the resulting potential V are sketched in the figure for each of the six regions delimited by the thin solid lines in the ξ – ℓ_D plane. All these lines meet for $\ell_D = \xi = \xi^*$, where we introduce $\xi_c \equiv [Ae\ell_\sigma/(2\sigma)]^{1/3} \simeq 1 \text{ nm}$ and define ξ_c^* via $(\xi_c^*/\xi_c)^3 g^2(\xi_c^*/\ell_\sigma) = 1$ which renders $\xi_c^* \simeq 1.8 \text{ nm}$ for the present experiment. In order for the above model of $V = V_{\text{el}} + V_C$ to be consistent, it is necessary that the distances typically sampled by the aggregating colloids, *i.e.*, close to the position l_{min} of the minimum of $V(l)$, are in the range $R \gg l_{\text{min}} \gtrsim \xi, \ell_D$ so that the above expressions for V_{el}, V_C are applicable. These three conditions, delimit-

ited by the thick dashed lines in the figure, are satisfied



within the enclosed hatched area. In addition, the potential depth $V_{\text{min}} \equiv V(l_{\text{min}})$ — which, for fixed ξ , gradually increases upon decreasing $\ell_D < \xi$ [see the solid and dash-dotted lines within the hatched area, corresponding from top to bottom to $-V_{\text{min}}/(k_B T) = 0.1, 3, 10$] has to be large enough to cause the aggregation of the particles. This requires $V_{\text{min}} \lesssim -E_{\text{ACT}} \simeq -3k_B T$ [1]. Within the hatched area, this condition is fulfilled only in its cross-hatched part, which is significantly smaller than the region $\xi < \ell_D$ indicated in Ref. [1] and therefore it does no longer agree with the experimentally determined aggregation line [1] (data points in the figure).

Thus a careful study of the model proposed in Ref. [1] shows that it does not predict aggregation to occur at $\xi = \ell_D$, leading to a discrepancy with the reported data. Such a discrepancy is particularly significant at values of $\xi \gg \xi_0$ for which an interpretation in terms of universal critical phenomena could be acceptable.

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- [1] D. Bonn *et al.*, Phys. Rev. Lett. **103**, 156101 (2009).
- [2] A. Gambassi *et al.*, Phys. Rev. E **80**, 061143 (2009); C. Hertlein *et al.*, Nature **451**, 172 (2008).
- [3] J. Israelachvili, *Intermolecular and Surface Forces*, 2nd ed (Academic, London, 1992).
- [4] P. K. Madhavan Unni, J. Chem. Phys. **124**, 054505 (2006).
- [5] B. M. Law, J.-M. Petit, and D. Beysens, Phys. Rev. E **57**, 5782 (1998).
- [6] Landolt-Börnstein IV/17: Static Dielectric Constants of Pure Liquids and Binary Liquid Mixtures (Springer, Berlin, 2008).
- [7] MP and HW at $T \simeq 310 \text{ K}$ have mass densities $0.94 \text{ g}/\text{cm}^3$ and $1.1 \text{ g}/\text{cm}^3$, respectively [W. Marczak, J. Chem. Eng. Data **41**, 1462 (1996)].